VIBRONIC EMISSION SPECTROSCOPY OF JET-COOLED BENZYL-TYPE RADICALS FROM CORONA DISCHARGE OF CHLORO-SUBSTITUTED O-XYLENE MOLECULES

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Whereas benzyl radical, a prototypic aromatic free radical, has been the subject of numerous spectroscopic studies, chloro-substituted benzyl radicals have received less attention, due to the difficulties associated with production of radicals from precursors. The weak C-Cl bond can be easily dissociated in corona discharge of high voltage, leading to the formation of other benzyl-type radicals. During past years, we have concentrated the spectroscopy of chloro-substituted methylbenzyl radicals produced from corona discharge of precursor seeded in a large amount of helium carrier gas using a pinhole-type glass nozzle in a technique of corona excited supersonic expansion. From the analysis of the spectrum observed, we can easily distinguish the origin bands in the $D_1 \rightarrow D_0$ transition of the isomeric chloro-substituted methylbenzyl radicals with the additivity rule, [a] [b]discovered from the analysis of a series of benzyl-type radicals. Also, the displacement of phenylic Cl by benzylic H was confirmed to be dependent on the distance between Cl and H atoms. The benzyl-type radicals produced in corona discharge from precursor were determined based on the bond dissociation energies and molecular structure of precursor molecules as well as the agreement of the observed with the calculated ones from Gaussian program, from which the 2-methyl-3-chlorobenzyl, 2-methyl-4-chlorobenzyl, 2-methyl-5-chlorobenzyl, and 2-methyl-6-chlorobenzyl radicals were newly identified.

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[a] Y. W. Yoon, C. S. Huh, and S. K. Lee, *Chem. Phys. Lett.* **525-526**, 44-48 (2012).
[b] Y. W. Yoon and S. K. Lee, *J. Phys. Chem. A* **117**, 2485-2491 (2013).